

Preliminary Amendment  
U.S.S.N. 10/621,079  
Page 15 of 15

### REMARKS

This preliminary amendment corrects an unintentional and inadvertent printing error that occurred when the original version of the application was printed for filing. Support for the amendment to the specification comes from the priority Provisional Application – incorporated by reference. Accordingly no new matter has been added to this application by virtue of this preliminary amendment.

Correction of the specification is respectfully requested.

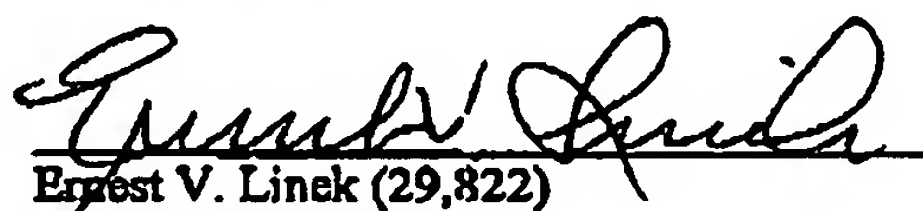
### FEE AUTHORIZATION

Please charge any fees due in connection with this filing to our Deposit Account – No. 19-0733.

### CERTIFICATE OF FACSIMILE TRANSMISSION

The undersigned hereby certifies that this correspondence was submitted by facsimile in the USPTO on the date shown on Page 1.

Respectfully submitted,

  
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1

# METHOD AND APPARATUS FOR REAL TIME MONITORING OF ELECTROPLATING BATH PERFORMANCE AND EARLY FAULT DETECTION

## PRIORITY CLAIM

[0001] This application claims priority from commonly owned, co-pending U.S. Provisional Application Serial No. 60/397,133, filed 19 Jul. 2002, the disclosure of which is hereby incorporated herein by reference.

## FIELD OF THE INVENTION

\* [0002] The present invention relates generally to any plating solution and methods for monitoring its performance. More specifically, the present invention relates to plating baths and methods for monitoring their plating functionality based on chemometric analysis of voltammetric data obtained for these baths. More particularly, the method of the present invention relates to the application of numerous chemometric techniques to describe quantitatively plating bath functionality in order to maintain proper performance of the baths. (text missing or illegible when filed) shock, depend on concentrations of constituents. Should the constituents fall outside of required concentration ranges, however, the bath may fail to satisfactorily perform its plating function. It is therefore important that deliberately added constituent concentrations are regularly and accurately monitored. Current techniques for plating bath components analysis, recently reviewed by Wildel et al. [1], do not employ reliable calibration methods employing multivariate data analysis capable of detecting outliers.

[0003] Unfortunately, most organic additives undergo degradation reactions, which lead not only to the depletion of their concentration but also to the introduction of degradation products in the plating bath. These degradation products accumulate and some of them impede the performance of plating bath. The degradation of polyoxyethylene-based surfactants (like the carrier in a copper plating bath) was discussed by Donbrow [2]. Possible degradation processes of brightener and carrier for copper plating baths were suggested by Dietz [3]. He concluded that the dosing logic for carrier based on the charge that flows through the plating solution cannot be correlated with carrier depletion. Dietz listed several contaminants that interfere with the brightener function: foreign metal contaminants, wetting agents from upstream cleaning operations, pre-plate microetchants, and materials leaching out of photoresists. Another possible foreign contamination are remains of hydrogen peroxide used for plating tank leaching and/or carbon treatment cycles.

[0004] None of the current techniques for plating bath components analysis, reviewed by Wildel et al. [1], deal with bath contamination at all, assuming performance of plating bath being equal to the freshly prepared plating solution.

[0005] The only existing method of checking the plating bath performance based on the visual examination of the deposit is Hull cell test that cannot be performed with in-tank electrochemical sensors. Two different sets of equipment must therefore be maintained in order to perform constituent analysis and contamination detection, as those two factors determine proper performance of the plating bath. No integrated measurement system is available which is capable of measuring constituent concentrations and of detecting bath contamination. Additionally, the major draw-

back of the Hull cell test is its capability to detect bath contamination only after the plating performance is already impeded. There is no existing technique for early detection of plating bath contamination that would enable execution of proper counter measurements before the plating performance is affected by the presence of contaminants.

[0006] Early detection of bath malfunctioning is crucial to avoid losses especially in the electronic industry where the cost of silicon wafers plated with defects may be sometimes measured in hundreds of thousands dollars. Recently implemented to the semiconductor manufacturing copper damascene plating process is especially sensitive to any unexpected perturbation. This includes not only any deviation from a very tight process specification, but also an extremely difficult to control accumulation of organic additive breakdown products. A complex structure on wafer surface (consisting of sub-micrometer size features—vias and trenches) has to be filled-in with copper with no defects, during the deposition step. The ability of the copper plating bath to fill-in this kind of small feature depends very much on the ratio of the organic additives—suppressors and accelerators. The mechanism of curvature enhanced accelerator coverage was proposed to explained superfilling properties of the electrolyte [4-7]. A pronounced hysteresis is observed in the copper voltammogram taken for the solution with such superfilling properties. But it is well known that the breakdown products of the accelerator can display either acceleration and/or suppression effect, while breakdown products of suppressors will be showing suppression effects of various strength. Thus the performance of a plating bath can be impeded severely because of such additional, and not controlled by any means, effects. Plating problems can be observed in solution with accumulated breakdown products, even when the deliberately added components of plating bath, measured by any analytical method, are within the specification range. Thus, even the accurate analysis of all of the target components may be not enough for the good performance of a plating bath.

[0007] The harmful effect of accumulated degradation products will be very dependent on the process specification and the size of features to be plated. Certain level of breakdown products can be fully acceptable for plating 0.25-micron features, while the same amount can produce defective parts when plating 0.13-micron or smaller gaps. In order to keep good bath performance, a renovation process called bleed-and-feed was introduced into the plating practice for semiconductor manufacturing. Every certain amount of time, a portion of the plating solution is removed from the tank and replaced with a freshly-prepared, contamination-free plating bath. This process is done without any analytical control. Thus, very often this procedure is performed unnecessarily, causing a total waste of still good (and also expensive) plating solution.

[0008] There is no simple and straightforward analytical method to evaluate the effect of degradation products of organic additives. So it is apparent that there presently is a need for a fast and inexpensive method capable of monitoring bath performance and/or early detection of plating problems.

## SUMMARY OF THE INVENTION

[0009] Disclosed is a process to produce a predictive data set which can be used to predict the property of a plating solution, said process comprising:

## PROVISIONAL PATENT APPLICATION

Docket No. 004522/00010

**METHOD AND APPARATUS FOR REAL TIME MONITORING OF  
ELECTROPLATING BATH PERFORMANCE AND EARLY FAULT DETECTION****FIELD OF THE INVENTION**

The present invention relates generally to any plating solution and methods for monitoring its performance. More specifically, the present invention relates to plating bath and methods for monitoring its plating functionality based on chemometric analysis of voltammetric data obtained for these baths. More particularly, the method of the present invention relates to application of numerous chemometric techniques to describe quantitatively plating bath functionality in order to maintain its proper performance.

**BACKGROUND OF THE INVENTION****Sources of Improper Performance of Plating Bath**

A typical plating bath solution comprises a combination of several different chemical constituents. The specific constituents vary depending upon the type of plating bath. The concentration levels of constituents are important determinants of the quality of the resultant plating deposit. The characteristics of the plating deposit, including tensile strength, ductility, solderability, uniformity, brightness and resistance to thermal